Paper-based Energy Storage Devices

Ian Robertson Literature Seminar November 7, 2013

Paper has been used as the substrate of choice for information storage and transmission for over 2000 years in the form of writing. In the past decade, there has been a large amount of research focused on using paper as a substrate for the technology age. Whitesides has developed a variety of paper-based bioanalytical devices and the Rogers group have developed a variety of electronics that can rest on paper substrates.[1,2] These paper-based devices are extremely flexible, inexpensive, and have potential applications in clinical diagnostics, bendable displays, and biosensing. Flexible electronics such as these require a power source, but currently have to resort to rigid lithium-ion batteries, which limits them in terms of portability and biocompatibility. Recently, paper has been explored as a matrix for the storage of electrical energy to provide solutions to these difficulties. To understand why paper is being sought as a substrate for both electronics and power sources, it is important to understand the properties that paper possesses that make it so useful, viz. low cost, high strength, and high porosity.

Paper is composed of cellulose fibers, typically derived from living organisms. Since cellulose is the most abundant organic substance on the planet, paper can be purchased for ca. $0.10 per square meter – an extraordinarily low cost.[3] In large scale applications or for products used in impoverished areas of the world, cheap materials are a key factor for practical use.

The high strength of cellulosic paper is derived, on a fundamental level, from both its chemical structure and its larger nanostructure. Cellulose is a linear polymer of D-glucose and is synthesized by a wide variety of land plants and algae as well as some bacteria. Depending on the source and processing method, the polymer chains can be aggregated into larger fibrils of a variety of sizes. The cellulose molecules organize into crystalline regions, which then aggregate into nanofibrils. In land plants, these nanofibrils then form larger bundles, which further combine into wood fibers (**Figure 1**).[4] Paper is obtained by mechanically shearing the wood fibers to

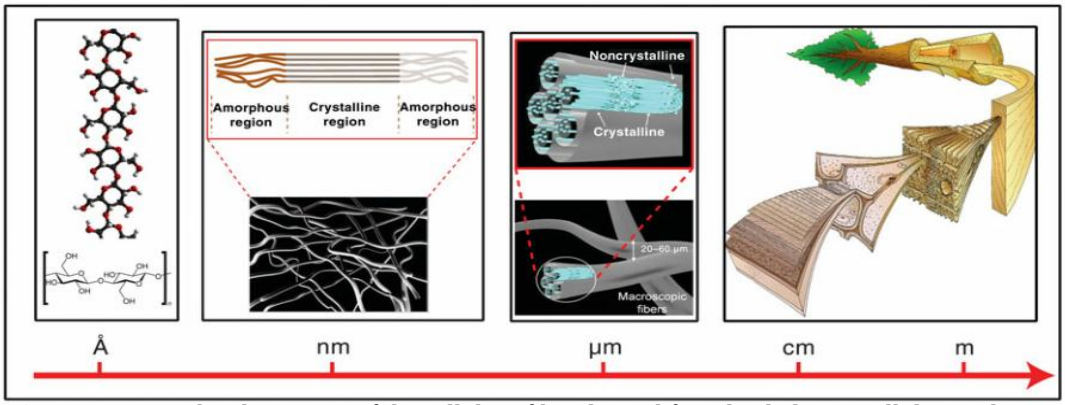

Figure 1: Hierarchical structure of the cellulose fiber derived from land plants. Cellulose polymer (left) assembles into nanofibrils, and microfibers, to produce the wood fibers found in the cell walls of trees (right).[4]

separate them into microfibers or nanofibrils, enzymatically treating to prevent reassembly back into the larger units, and pressing them into a thin sheet.[5] The many alcohol groups on glucose result in a high degree of hydrogen bonding that holds the cellulose fibers together tightly. This allows it to form porous networks while maintaining its high strength.[6]

The two main types of energy storage devices that are investigated in this area are lithium ion batteries (LiBs) and supercapacitors (SCs). LiBs store their energy in the form of the

electrochemical potential of reduced lithium atoms intercalated into a non-lithium matrix. Energy is then released through the oxidation of lithium.[7] SCs work by a different mechanism. SCs have no dielectric separating the charged layers; instead, they store energy through redox reactions occurring on the electrode surface and through charge separation in a Helmholtz double layer at the interface. Both LiBs and SCs are dependent on a large surface area on which to perform redox chemistry or maintain a double layer.[8]

The high porosity of cellulose, combined with its other benefits, lends itself well to acting as a scaffold for these energy storage devices. However, given that cellulose is nonconductive, additional functionalization in required in order to make it a useful material. The two methods discussed here will be the infiltration of paper by a charge holding material such as carbon nanotubes (CNTs) and the coating of individual cellulose fibers by a conducting polymer.

The first example of integrating CNTs into cellulose-based energy storage devices was by Pushparaj et al. in 2007, where they used the nanotubes themselves as the active electrodes.[9] Cellulose was introduced by solvation in a room-temperature ionic liquid and dispersion over a nanotube-covered surface. The ionic liquid was then evaporated, leaving behind a nanocomposite unit composed of CNT-suffused cellulose, soaked in an ionic liquid. Two of these units could be put together to form a SC or a single unit could be attached to a lithium electrode to form a battery. The main disadvantage of this approach is that CNTs are not optimal for reversibly intercalating lithium ions, causing the capacity to decay rapidly. Also, it requires the use of ionic liquids, which are expensive and very difficult to evaporate.

To remedy some of these problems, a new approach was taken by Hu et al. in 2009, where they used the carbon nanotubes as current collectors instead of active material. The nanotubes were dispersed in an ink solution to infiltrate standard printer paper and make it highly conductive. Metal nanoparticles of different composition were then integrated as electrodes.[10] This approach yielded a more stable storage device with a straightforward fabrication method. The use of standard printer paper as a substrate shows that any porous cellulose is sufficient. The ink was composed of an aqueous solution of CNTs with surfactant to enable better dispersion. Cellulose's high porosity and hydrophilicity cause the aqueous solution to penetrate all areas of the nanoscale network, leaving behind a conformal coating of CNTs after solvent evaporation (**Figure 2**). The high amount of contact area between CNTs and cellulose substrate results in tight binding due to van der Waals forces. Thus, there is no delamination of CNTs even when an adhesive tape is applied. Once again, the mechanical properties of cellulose allow the device to have flexibility and strength while maintaining good electrical properties.

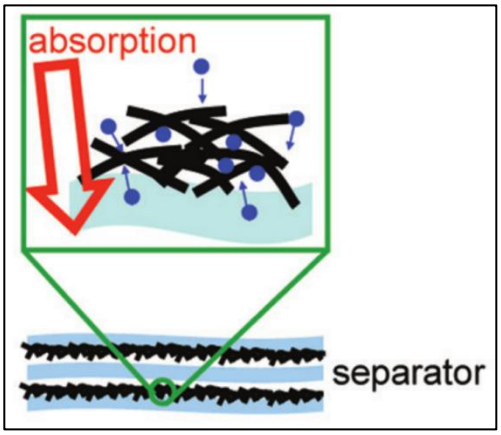

Figure 2: A CNT/paper supercapacitor. Two sheets of CNT-coated paper surround filter paper soaked in electrolyte. Inset shows easy access of electrolyte ions to CNT surface due to cellulose porosity.[10]

Both approaches exploit cellulose's high porosity and intrinsic surface area to allow for higher capacity energy devices. They also use the high strength of cellulose to allow the devices to be flexible, yet possess robust mechanical properties. The SC application of the nanotube-based devices relies almost exclusively on double-layer charging, since the nanotubes do not readily perform redox chemistry. In order to take advantage of both kinds of capacitance, a different approach is to utilize conducting polymers as current carriers by integrating them into the porous paper structure. Polymers like polypyrrole can become p-doped through oxidation, and intercalate anions into their chemical structure.[11] By acting as charge holders as well as

reactive surfaces, polymer electrodes have a theoretically higher capacitance than materials that only hold charge.[12] Thus, if such a polymer were able to be made highly porous, it could have advantages over the CNT approach.

The approach taken by Nystrom et al. in 2009 involves performing a polymerization of pyrrole on the surface of a cellulose cake.[13] Pyrrole's hydrogen bonding causes it to polymerize as a coating on the nanoscale cellulose fibers (**Figure 3**). The fibers are then formed into a sheet of paper-like material. When charging the SC, the polypyrrole is reduced to its neutral form, pushing chloride anions out of its matrix. Conducting polymer-based SCs have a significantly faster charging and discharging rate, due to the rapid diffusion of anions into and out of the nanostructured matrix. However, conducting polymer ESDs have difficulty reaching voltages much higher than one volt and are prone to self-discharge. More fundamental research will be required before this strategy is truly viable.

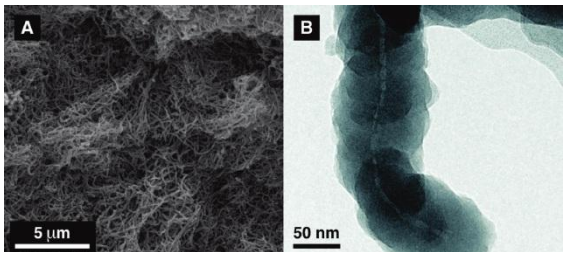

Figure 3: Electron micrographs of polypyrrole-coated cellulose nanofibrils. **(A)** SEM image of highly porous structure obtained with polymer coating. **(B)** TEM image of a single cellulose nanofibril coated in polypyrrole.[13]

Paper is a strong candidate as a useful substrate for energy storage in flexible electronic devices. The incorporation of CNTs and conducting polymers provide promising potential avenues for this field. The future of these systems lies in optimization and innovation. Improvements in fine tuning the structure of the cellulose matrix would likely improve electrochemical performance of the energy storage devices through improved surface area or more uniform structure. Cycling stability and capacity for these systems is not yet competitive with industrial standards of traditional LiBs and SCs, and, given the limitations that flexibility presents, this deficiency will persist. Nevertheless, advances in the fields of Li-ion batteries, conducting polymers, and CNTs will provide better performance in these paper power sources. It seems likely that, as flexible electronics become ever more commonplace, paper will continue to impact our lives in increasingly technological ways.

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